19

Soil pH and pH Buffering

19.1 Introduction **19**-1
19.2 Definition and Determination of Soil pH **19**-1
Definition of pH • Determination of pH with Electrodes • Determination of Soil pH Using pH-Sensitive Dyes
19.3 Acids and Bases in Soil Solutions **19**-3
Weak Acids • Weak Bases
19.4 Overview of Reactions Controlling pH and pH Buffering **19**-4
19.5 Buffering by Soil Organic Matter **19**-5
19.6 Proton and Al Exchange in Silicate Clays **19**-7
19.7 pH-Dependent Charge Buffering by Mineral Components **19**-7
Oxides and Hydroxides of Iron and Aluminum • pH-Dependent Charges on Silicate ClayEdges • Imogolite and Allophane
19.8 Buffering by Dissolution and Precipitation of Carbonates **19**-9
19.9 H^+ Consumption by Irreversible Weathering of Aluminous Minerals **19**-9
Weathering of Primary Silicates • H^+ Consumption by the Destruction of High-Activity Clay
19.10 Determination of Buffer Capacities **19**-10
Total Titratable Acidity • Lime Requirement • Calcium Carbonate Concentrations in Soil • Determination of the Buffering of H^+ Inputs in Noncalcareous Soils
19.11 Soil Acidification **19**-11
Natural Acidification • Acid Rain • Acid-Producing Fertilizers • Acidification by Sulfur Compounds
References **19**-12

Paul R. Bloom
University of Minnesota

Ulf Skyllberg
Swedish University of Agricultural Sciences

19.1 Introduction

Soil pH is a measure of soil acidity or alkalinity and is probably the single most important chemical characteristic of a soil. In the past, soil acidity or alkalinity, reported in pH units, was also referred to as "soil reaction" (Mason and Obenshain, 1939), and this term is occasionally still used in some publications. However, "soil reaction" is no longer used by soil chemists (SSSA, 2008). Because of the importance of acidity and alkalinity in soils, pH has been called a master variable (McBride, 1994), with knowledge of soil pH required to understand many chemical processes including ion mobility, precipitation and dissolution equilibria and kinetics, and oxidation–reduction equilibria. Soil pH also affects nutrient availability to plants and the negative response of many plant species to soil acidity.

Soils are a complex mixture of solid-phase components that react to yield a measured pH value. These components also buffer soils against pH changes caused by natural and anthropogenic inputs of acids and bases. Knowledge of the reactions that buffer soil pH is necessary for an understanding of natural soil weathering and the response of a soil to inputs of lime, acid-forming N fertilizers, acid-mine wastes, and acid rain. The discussion in this chapter focuses on the reactions of components that buffer soil pH in upland soils. Factors affecting pH and buffering in flooded soils are discussed in Chapter 14.

19.2 Definition and Determination of Soil pH

Because pH is a term that is only defined for solutions, in a strict sense, it cannot be applied to a solid-phase material like soil. However, the chemical properties of the solid-phase components in soil define the pH of the soil solution, the water in soil pores (Chapter 12).

19.2.1 Definition of pH

The term pH was defined by Sorensen (1909) to provide a convenient way of representing the H^+ or OH^- concentrations in aqueous solutions. As currently defined, pH is the negative logarithm, base 10, of H^+ activity, log (H^+), where activity is the concentration adjusted for nonideality caused by charge–charge interactions with other ions in solution. In all except saline soils, the ionic interaction correction is small and the difference between

H^+ concentration and activity is small. The determination of H^+ also provides a measurement of OH^- in solution. At 25°C in pure water, the relation between OH^- activity, (OH^-), and H^+ activity, (H^+), is given by

$$K_w = (H^+)(OH)^- = 1.0 \times 10^{-14} \quad (19.1)$$

where K_w is the ionization constant for water. Expressing Equation 19.1 as negative logarithms yields

$$pH + pOH = 14 \quad (19.2)$$

where pOH is the negative logarithm of the OH^- activity.

19.2.2 Determination of pH with Electrodes

Soil pH is determined by measuring the pH after equilibrating soil with pure water or a salt solution (SSSA, 2008). The pH of a solution in equilibrium with a soil varies with the composition and concentration of the salts in the solution because cations in solution displace H^+ and Al^{3+}, an acidic cation, from soil surfaces. Three common standard methods for determining pH in soils involve the suspension is distilled water, 0.01 M $CaCl_2$ or 1 M KCl solutions, and measurement of the solution pH in the solution (Thomas, 1996). In the United States, the most commonly reported pH measurements are in 1:1 (weight:volume) suspensions of air-dried soil in distilled water. A suspension of soil is prepared (e.g., 10 g of soil and 10 mL of distilled water), stirred vigorously, and then allowed to stand for 10 min. The suspension is stirred again and the pH is measured with a glass pH electrode and a pH meter (Thomas, 1996). The pH can also be measured with an ion-sensitive field-effect transistor (ISFET) electrode. These solid-state devices are more robust than glass electrodes, have a more rapid response, and are well adapted for making field measurements of soil pH (Rossel and Walter, 2004). However, the solid-state electrodes are more expensive than glass electrodes.

The determination of soil pH in a 1:1 water suspension is expected to give a higher pH value than the soil solution at field water contents. The quantity of water added results in a dilution of the salts in the soil solution and a lower-equilibrium salt concentration. This effect is illustrated by the 0.4 unit increase in pH obtained for an increase in water content in the soil suspension from 1:1 to 1:10 (Thomas, 1996). The 1:1 water determination of pH is influenced by the natural seasonal variation in soil solution salt concentrations and the effects of soil management; for example, recent fertilization. Soil pH measured in water is reported as $pH_{(H_2O)}$ or pH_w.

At low salt concentrations, an error due to the junction potential effect can occur in determination of $pH_{(H_2O)}$. A pH measurement requires contact with the solution by a glass electrode and a porous liquid junction of a reference electrode. This is necessary to complete the circuit between the pH-sensitive glass electrode and the reference electrode, which is often built in the same body as the glass electrode to form a combination electrode. The filling solution for the reference electrode is a concentrated KCl solution, which slowly leaks into the test solution through a porous liquid junction. Because soils are cation exchangers, they can have a disproportionate effect on the rate of K^+ diffusion compared to Cl^- diffusion into solution, which sets up a potential across the junction (Coleman et al., 1951). This can cause a reduction in the measured pH (Thomas, 1996).

The method for measurement of pH in 0.01 M $CaCl_2$ is the same as for measurement of pH in distilled water (Thomas, 1996). Because of the displacement of H^+ and Al^{3+} from soil materials by Ca^{2+}, pH in 0.01 M $CaCl_2$ [$pH_{(CaCl_2)}$] is on an average about 0.3–0.4 units lower than in water (Essington, 2004). The measurement of pH in 0.01 M $CaCl_2$ results in reduction or elimination of the problems due to variation in soil solution salt concentration and it eliminates the junction potential effect. Calcium is used in the determination of pH because it is the predominant soil solution cation in soils of temperate regions. The 0.01 M concentration, however, is somewhat higher than that found in most soil solutions.

The measurement of pH in 1 M KCl suspensions also generally yields lower pH values than in water. However, for some subsurface horizons of highly weathered soils of the tropics, pH in KCl can actually be greater than in water (van Raij and Peech, 1972). This occurs in subsoils low in permanent charge silicate clays and low in organic matter. Oxides and hydroxides of iron and aluminum are the predominant ion exchangers in these soils and at very acid pH values they are anion exchangers (Section 19.7). The addition of KCl results in a displacement of OH^- by Cl^- and an increase in pH (McBride, 1994).

19.2.3 Determination of Soil pH Using pH-Sensitive Dyes

Rapid determination of soil pH can be made colorimetrically with pH indicator dyes. Colorimetric methods are based on the change in color that takes place upon disassociation of a weak acid or a weak base organic dye. In solution, a weak acid dye molecule can dissociate:

$$HI = H^+ + I^-. \quad (19.3)$$

An increase in pH will cause a change in color as the undissociated dye, HI, changes to the dissociated form, I^-. Typically a mixture of dyes is used to yield color changes that take place over a wide range of pH. A dye solution is mixed with soil to make a slurry, and the dye is decanted from the soil so the color can be compared with a color chart. The pH measured in this manner corresponds with $pH_{(H_2O)}$ measured with a glass electrode but is not as precise and can vary from the glass electrode results by as much as 0.4 units (Mason and Obenshain, 1939). Dye-impregnated pH papers also can be used to get quick pH measurement within 0.5 units of the true $pH_{(H_2O)}$ (Thomas, 1996).

19.3 Acids and Bases in Soil Solutions

Soil solutions contain a mixture of weak acids and weak bases that buffer the pH of the solution. This buffering is small compared to the quantity of acidity or basicity (alkalinity) associated with the solid phases in soil and has little impact on soil pH buffering. However, the acid and base components in soil solutions directly impact plant roots and soil microbes and thus directly influence the vitality of the biotic community in a soil. Also, the acids and bases in soil solution directly impact mineral weathering and biogeochemical reactions involved in soil genesis.

In this chapter, we will use Brønsted's definition of acids and bases where an acid is a hydrogen ion (H^+) donor and a base is an H^+ acceptor (Stumm and Morgan, 1996). Because an H^+ ion is just a proton, acids can be described as proton donors and bases as proton acceptors. According to this definition, reaction of an acid to lose a proton produces a conjugate base that can accept a proton; if the reaction is reversed. Conversely, a base that accepts a proton yields a conjugate acid. For example, when nitric acid donates protons to water, the base is H_2O. The reaction is

$$HNO_3 + H_2O = NO_3^- + H_3O^+. \tag{19.4}$$

The nitrate anion is the conjugate base of nitric acid and the hydronium ion, H_3O^+, is the conjugate acid of water. Nitric acid is a strong acid because at all except very high H^+ concentrations Reaction 19.4 goes all the way to the right and all of the HNO_3 is ionized. The conjugate base of nitric acid, the nitrate anion, is a very weak base because it has very little tendency to accept protons. The above reaction in aqueous solution is often abbreviated to

$$HNO_3 = NO_3^- + H^+. \tag{19.5}$$

19.3.1 Weak Acids

The weak acids in soil solutions include organic carboxylic acids, H_2CO_3, and Al^{3+}, a metal ion that undergoes hydrolysis. Carboxylic acids are organic compounds with one or more –COOH groups that have the potential to ionize to form the carboxylate anion, $RCOO^-$, according to the reaction

$$RCOOH = RCOO^- + H^+ \tag{19.6}$$

where
RCOOH is any carboxylic acid
R is an organic structure

Organic acids in soil solutions include simple acids like malic acid $(COOH)CH_2CH(OH)CH_2(COOH)$ and citric acid $(COOH)CH_2C(OH)(COOH)CH_2(COOH)$, which are exuded from plant roots or by soil microbes. These acids generally have a short lifetime in soils because they are easily consumed by soil microbes. In addition, soil solutions contain macromolecular humified components produced by degradation of plant debris that can be operationally separated into humic and fulvic acids (Chapter 11; Stevenson, 1994), with fulvic acids predominating in soil solutions. These natural organic acids are complex mixtures that contain carboxylic acid groups.

The strength (ability to donate protons) of a carboxylic acid is defined by the equilibrium constant:

$$K_a = \frac{(RCOO^-)(H^+)}{RCOOH} \tag{19.7}$$

where K_a is the acidity constant. Stronger acids have greater acidity constants. Often, the strength of a weak acid is given in terms of the negative log of the K_a, the pK_a. The lower the pK_a the greater the strength of the acid. At the pH equal to the pK_a, an acid is half ionized. At higher pH, it is more than half ionized, while at lower pH it is less than half ionized. Thus, at solution pH values less than the pK_a, a weak acid has a greater ability to donate protons than at higher pH values. Carboxylic acids in soil solution have pK_a values generally in the range of 3–5.

The soluble fulvic acids also contain phenolic groups, ArOH, where Ar is an aromatic six-carbon ring structure. Phenolic groups are generally much less concentrated than the carboxyl groups and they are much less acidic having pK values ranging from 7 to 11.

The Al^{3+} ion can be an important weak acid component in soil solutions of highly acid soils. This ion contributes to soil solution acidity and causes the acid toxicity response experienced by many plants in acid soils (Bloom et al., 2005; Fageria and Baligar, 2008). In water, Al^{3+} undergoes a series of hydrolysis reactions, which produce protons (Nordstrom and May, 1996):

$$Al^{3+} + H_2O = AlOH^{2+} + H^+ \quad pK_{a1} = 5.00, \tag{19.8}$$

$$AlOH^{2+} + H_2O = Al(OH)_2^+ + H^+ \quad pK_{a2} = 5.1, \tag{19.9}$$

$$Al(OH)_2^+ + H_2O = Al(OH)_3^0 + H^+ \quad pK_{a3} = 6.7, \tag{19.10}$$

$$Al(OH)_3^0 + H_2O = Al(OH)_4^- + H^+ \quad pK_{a4} = 6.2. \tag{19.11}$$

Although the second, third, and fourth hydrolysis reactions are important in determining the chemistry of Al, only the first hydrolysis reaction is a major source of protons in soil solution. The low solubility of solid $Al(OH)_3$ limits the quantity of Al ions. At a pH of 5.0, a solution in equilibrium with $Al(OH)_3$ has a total concentration of Al^{3+} of less than 10^{-6} M (Nordstrom and May, 1996).

In soils, carbonic acid is also an important weak acid (H_2CO_3) that is created by the dissolution of carbon dioxide:

$$CO_{2(g)} + H_2O = H_2CO_3 \quad pK = 1.51 \text{ (Stumm and Morgan, 1996).} \tag{19.12}$$

When pH is increased, this acid ionizes to produce bicarbonate and H^+:

$$H_2CO_3 = HCO_3^- + H^+. \quad (19.13)$$

The pK_a for Reaction 19.13 is 6.35 (Stumm and Morgan, 1996) meaning that carbonic acid is a weaker acid than organic carboxylic acids or Al^{3+}. The concentrations of HCO^- in solution increase both with increase in pH and increase of concentration of CO_2 in the air of soil pores. At a pH value above 6, HCO_3^- is often the predominant anion in soil solution.

For solutions in equilibrium with the earth's atmosphere, H_2CO_3 is directly proportional to the partial pressure of atmospheric CO_2, which in 2007 was 3.83×10^{-4} atm. The concentration is increasing at the rate of 0.014×10^{-4} atm year^{-1} (Anon, 2008). However, in soils where root and microbial respiration are active, the partial pressure can easily be 100 times greater (Fernandez and Kosian, 1987; Magnusson, 1992). This has a great effect on the content of HCO_3^- in soils (Andrews and Schlesinger, 2001).

19.3.2 Weak Bases

All of the anions of the weak acids above, as well as the hydrolyzed Al cations, are weak bases that can accept protons in the pH range found in soils. Because of the low pK_a values for organic acids and $AlOH^{2+}$, these ions are only important proton acceptors in very acid soils. For most neutral and alkaline soils, the concentration of bicarbonate determines the alkalinity of soil solutions, where alkalinity is defined as the quantity of strong acid needed to lower the pH of a solution to the end point for complete protonation of bicarbonate (about pH = 4.8) (Stumm and Morgan, 1996). The carbonate ion, CO_3^{2-}, is significant only in very high pH soils because the pK_a for the ionization of HCO_3^- to CO_3^{2-} is 10.33 (Stumm and Morgan, 1996).

Under some conditions, solution ammonia, $NH_{3(aq)}$, is a significant base. These conditions are induced by the addition of fertilizer N as anhydrous ammonia [$NH_{3(g)}$], or urea. When $NH_{3(g)}$ is injected into a soil, it reacts with the soil solution to lower the H^+ activity raising the pH. Ammonia is a conjugate base of NH_4^+ and if the reaction in water is written like the weak acid reactions above:

$$NH_4^+ = H^+ + NH_{3(aq)}. \quad (19.14)$$

The pK_a of this reaction is 9.5 (Stumm and Morgan, 1996) and in all except the highest pH soils, the reaction goes to the left consuming protons. This reaction creates localized pH values near anhydrous ammonia injection bands that can be >9.5 (Havlin et al., 2005).

Dissolution and hydrolysis of urea fertilizer in soils can also produce localized high concentrations of $NH_{3(aq)}$ that can result in localized high pH. Fertilizer granules hydrolyze readily due to the presence of urease enzymes in soils, resulting in an overall reaction:

$$\underset{\text{Urea}}{(NH_2)_2CO} + 2H_2O = HCO_3^- + NH_4^+ + NH_{3(aq)}. \quad (19.15)$$

The basicity effect of the NH_3-producing fertilizers is short-lived because biological oxidation of ammonium to nitrates produces two H^+ ions, and the net effect is acidification.

19.4 Overview of Reactions Controlling pH and pH Buffering

Reactions of the solid-phase components control soil pH and are the reactions that buffer soil pH against rapid pH change with natural or anthropomorphic inputs of acids and bases (Bloom et al., 2005). Solid-phase soil materials have a much greater capacity to accept or donate protons than the soluble acids and bases in soil solution. Magdoff and Bartlett (1985) investigated the buffering in 51 surface soils of Vermont, USA by reacting these soils with H_2SO_4 or $CaCO_3$ for 30 days and determining the final pH in 0.01 M $CaCl_2$. They found maximal buffering (minimal slope of pH vs. added acid or $CaCO_3$) to occur at both pH 3.5 or less and pH 7.5 or greater (Figure 19.1). The upper bound of the pH in the buffering shown in Figure 19.1 is fixed by the solubility of $CaCO_3$ (Magdoff and Bartlett, 1985). They also showed that the buffer plot was generally linear in the pH range of 4.5–6.5, a range that encompasses most acid agricultural soils.

The pH-buffering reactions in soils include proton desorption and adsorption reactions with mineral and organic components as well as ion exchange, dissolution, and precipitation. Some of the soil components are effective in buffering over a wide range of pH values, while others are effective over a limited pH range (Table 19.1). The buffer ranges in Table 19.1 are those that were developed by Bloom et al. (2005) and are somewhat similar to those shown

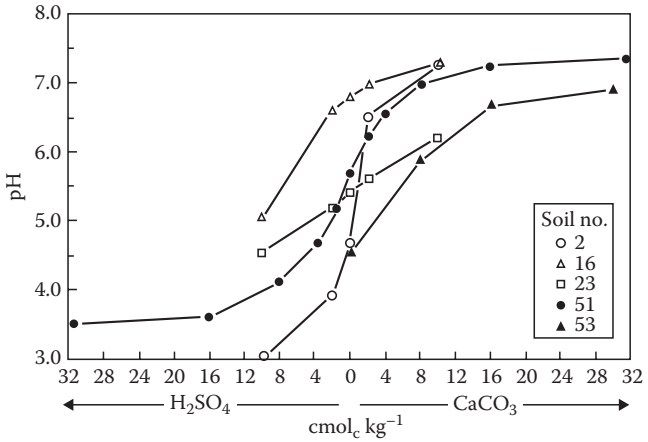

FIGURE 19.1 Titration of surface soils from Vermont, U.S.A, with H_2SO_4 and $CaCO_3$. The acid and base ($CaCO_3$) additions are reported per gram of soils. The pH_{CaCl_2} was measured after a 30-day reaction at field capacity moisture content. (From Magdoff, F.R., and R.J. Bartlett. 1985. Soil pH buffering revisited. Soil Sci. Soc. Am. J. 49:145–148. With permission of Soil Science Society of America.)

TABLE 19.1 Reactions of Solid-Phase Soil Components That Buffer pH in the Range of 3.5–9.5

pH Buffer Substance	pH Range	Proton Acceptor or Donation Reactions
Limestone, $CaCO_3$	7–9.5	Dissolution and precipitation
Oxides and hydroxides of Fe and Al; silicate clay edges	Whole pH range	H^+ adsorption and desorption on surface hydroxyl sites
H^+–SOM	Whole pH range	Dissociation and protonation of carboxyl and phenol groups
Al-SOM and $Al(OH)_{3(s)}$	5–8	Precipitation of organic bound Al^{3+} as $Al(OH)_3$ or dissolution of $Al(OH)_3$ by organic acids
Al^{3+}/H^+-exchange in SOM	Less than 4.5	H^+ exchange with Al^{3+} on carboxyl and phenol groups
$Al(OH)_3$	4–5.5	$Al(OH)_3$ dissolution/precipitation in soils with very low SOM content
Silicate clay interlayer $Al(OH)_n^{3-n}$ in 2:1 clays	4.2–7	Hydrolysis and precipitation or dissolution of interlayer $Al(OH)_3$
Permanent charge silicate clays	3.5–4.2	Ion exchange of H^+ and Al^{3+}
Irreversible dissolution of high-activity 2:1 silicate clays and poorly ordered aluminosilicates	Less than 3.5	Consumes H^+ upon release of Al^{3+} from reactive silicates
Very slow irreversible weathering primary silicate minerals	Whole pH range	Consumes H^+ upon dissolution of Ca^{2+}, Mg^{2+}, K^+, and Na^+ from primary minerals

Source: Bloom, P.R., U.L. Skyllberg, and M.E. Sumner. 2005. Soil acidity, p. 411–460. *In* A. Tabatabai and D. Sparks (eds.) Chemical processes in soils. SSSA, Madison, WI.

by Ulrich (1991), with modifications and additions. For example, Ulrich did not include soil organic matter (SOM) and reactions on oxide and hydrous oxide surfaces. The buffer reactions in Table 19.1 will be discussed in more detail in Sections 19.5 through 19.9.

19.5 Buffering by Soil Organic Matter

Soil organic matter is a very important component of pH buffering in surface soils, even in typical upland soils that contain only a few percent organic matter. Like the soluble organic components in soil solution discussed in Section 19.3.1, SOM contains carboxyl and phenolic groups that can donate protons. Most of the acidity in SOM is contributed by the humidified components, operationally defined as humic and fulvic acid. In soils, some of the weak acid sites exchange protons with Al^{3+}, which alters the proton donation behavior of SOM. Based on chemical analysis of humic and fulvic acids extracted from SOM (Chapter 11) various organic acids have been proposed to represent the acidity of carboxyl and phenolic sites in SOM. Most of the acidity is thought to arise from carboxyl and OH groups bound to aromatic ring structures, which can be represented by benzoic acid (Ar–COOH, pK_a = 4.2) and phenol (Ar–OH, pK_a = 10.0), where Ar is an aromatic ring (Smith et al., 2004).

Soil organic matter buffers pH over a wider range of pH values than predicted by a simple mixture of benzoic acid and phenol. The titration plots for two humic acids with an alkali metal hydroxide shown in Figure 19.2 illustrates that maximum buffering (minimal slope) is in the pH range of 4–6. At very low pH, the plots in Figure 19.2 have very low slopes because of the effect of dilution of acid on H^+ concentration as presented on a log (pH) scale. And at pH > 8.5, the buffering due to phenolic groups contributes to the low slope. A broadening of the buffering response occurs because the aromatic ring structures of the humic acid and fulvic acids are polysubstituted with carboxyl –COOH and phenolic –OH. This shifts the pK_a values, resulting in aromatic ring structures with wide ranges of individual pK_a values. Also, with the ionization of the acid sites, negative charges accumulate on

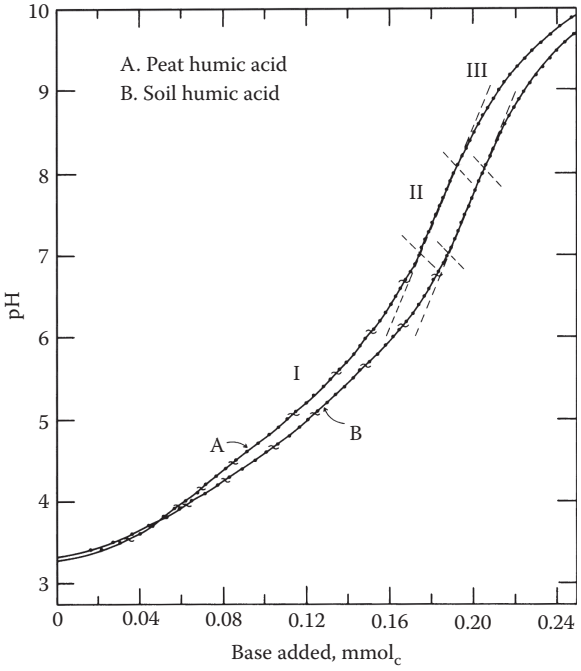

FIGURE 19.2 Titration of 2 humic acids with strong base. (From Stevenson, F.J. 1994. Humus chemistry: Genesis, composition, reactions, 2nd Ed. Wiley, New York. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. With permission.)

macromolecular structures and this charge reduces the proton donation ability of humic and fulvic acids at high pH values (McBride, 1994). The ionization of carboxyl groups is generally complete at pH 8 and the ionization of phenolic groups is complete at pH 11. Thus, common methods for determination of carboxyl acidity involve titrating to pH 8; and for the determination of the phenol titration to pH in excess of 11 (Stevenson, 1994). The negative charge sites produced by the ionization of the weak acid sites on humic and fulvic acids bind exchangeable cations. Organic matter contributes much of the pH-dependent cation exchange capacity (CEC) to soils (Chapter 16).

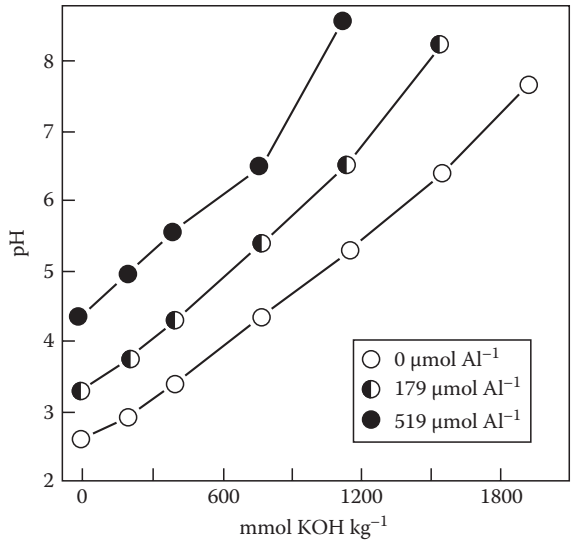

FIGURE 19.3 Titration of Al-SOM containing different contents of Al^{3+}. (From Hargrove, W.L., and G.W. Thomas. 1982. Titration properties of Al-organic matter. Soil Sci. 134:216–225. With permission of Wolters Kluwer Health.)

The binding of Al to acid functional groups in SOM is important both for Al chemistry and for pH buffering. In acid mineral soils, many of the carboxylate sites in SOM are bound to Al^{3+}. This bonding is strong enough that only a small fraction of the Al can be extracted with 1 M KCl (Bloom et al., 1979), and most authors consider Al (and H^+) bound to SOM to be nonexchangeable (Bertsch and Bloom, 1996). This strongly bound Al has a large effect on buffering. Hargrove and Thomas (1982) titrated SOM with varying Al^{3+} contents and found that the pH buffering of the Al^{3+}-treated SOM occurred at higher pH than for H^+-saturated SOM (Figure 19.3). Aluminum-saturated SOM is a weaker acid than H^+-saturated SOM.

As the pH of Al-SOM is raised to greater than about 5, the Al^{3+} in solution exceeds the solubility of $Al(OH)_3$ and precipitation of amorphous $Al(OH)_3$ occurs (Walker et al., 1990). This can be illustrated by

$$2Al(RCOO)_3 + H_2O = 3RCOO^- + 3H^+ + Al(OH)_{3(s)}. \qquad (19.16)$$

This reaction is reversible and when the pH is lowered $Al(OH)_3$ dissolves and Al again becomes bound to organic matter. As with H^+-SOM, increasing of pH by adding a base increases surface charge and the organic matter becomes more saturated with the cation of the base. In humic materials, except at very low pH, the pH is positively correlated with the saturation of cation exchange sites with the Ca^{2+}, Mg^{2+}, Na^+, and K^+; all cations of strong bases. In soil science, these are called "base cations" and a base saturation (BS) value, which is positively correlated to pH, can be calculated as a sum of charges of base cations divided by the CEC:

$$BS = \frac{2Ca^{2+} + 2Mg^{2+} + Na^+ + K^+}{CEC}. \qquad (19.17)$$

In this calculation, the CEC value is determined at a reference pH of 7 or 8 (Bloom and Grigal, 1985; Ross et al., 2008). In less-acidic and neutral soils, the most abundant base cation is Ca^{2+}.

As soils are acidified, base cations are displaced and the BS value decreases. At pH values less than 5, the BS is low and protons can displace soil adsorbed Al^{3+} ions. This reaction results in a decrease in pH without a decrease in BS because H^+-saturated SOM is a stronger acid than Al-saturated SOM. At pH less than 4.5, this exchange can add very significant quantities of Al^{3+} to soil solution. At these low pH values, where hydrolysis of Al^{3+} is not very significant Al^{3+} is acting more like a base cation. In the high acid A and O horizons typical of many forest soils of northern temperate and humid tropical regions, plots of BS vs. pH show a better positive correlation with BS when Al^{3+} is included as a base cation than if it is included as an acid cation (Skyllberg, 1994, 1999; Ross et al., 2008).

SOM provides much of the pH buffering in most surface soils and much of the CEC. Helling et al. (1964) estimated the mean CEC of SOM in 60 mineral soils of Wisconsin, USA, at pH 8, to be 2000 $mmol_c$ kg^{-1} of SOM. This value is the equivalent to the value for the titration of the acid form of organic matter with $Ca(OH)_2$ to pH 8 and provides a reasonable estimate for the capacity of SOM in mineral soils to buffer pH in the range of 3–8. With the exception of $CaCO_3$, the pH-buffering capacity of SOM is equal or greater than other components in the soil (Table 19.2). Another indication of the importance of SOM for buffering in soils is the results after adding H_2SO_4 and $CaCO_3$ to 51 surface soils (Magdoff and Bartlett, 1985). They took the data, including the four soils in Figure 19.1, and replotted it normalized to equivalent SOM contents. This yielded a single plot (Figure 19.4) for soils of differing organic matter contents suggesting that in these northern temperate region surface soils, the pH buffering is a function mostly of organic matter content.

TABLE 19.2 Approximate Maximum Proton Donation or Adsorption Capacity of Soil Materials in the pH Range of 3.5–8

Soil Material	Capacity, mmol kg^{-1}	References
Silicate clays		
Smectites	800–1,500	McBride (1994)
Vermiculite	1,500–2,000	McBride (1994)
Illite	200–400	McBride (1994)
Kaolinite	10–50	Thomas and Hargrove (1984)
SOM	2,000	Helling et al. (1964)
Allophane and imogolite	200–500	Wada (1989)
Hydroxides and oxides of Fe and Al[a]	50–400	Borggaard (1983)
$CaCO_3$[b]	20,000	Stumm and Morgan (1996)

[a] Based on linear extrapolation between pH 8 and 3.5 of the data for hematite and goethite.

[b] The precipitation and dissolution of $CaCO_3$ takes place at pH 7 or greater.

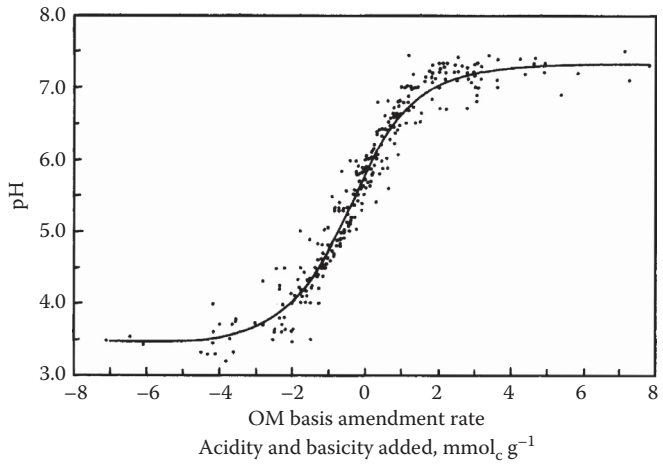

FIGURE 19.4 pH_{CaCl2} after a 30-day reaction of 51 soils from Vermont, U.S.A, with varying additions of H_2SO_4 and $CaCO_3$. The acid and base addition are reported per gram of SOM. The data for all of the soils were adjusted along the x-axis to coincide with the zero addition pH for soil 51 (see Figure 19.1). (From Magdoff, F.R., and R.J. Bartlett. 1985. Soil pH buffering revisited. Soil Sci. Soc. Am. J. 49:145–148. With permission of Soil Science Society of America.)

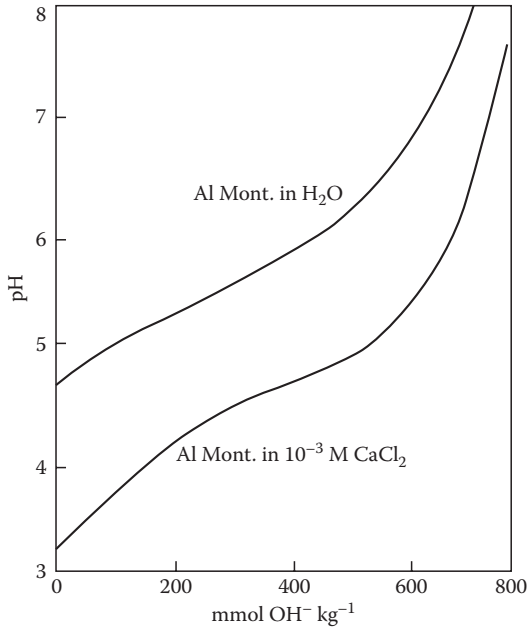

FIGURE 19.5 Titration of an Al saturated montmorillonitic clay with NaOH with and with without the addition 0.001 M $CaCl_2$. (From Turner, R.C., and W.E. Nichol. 1962. A study of the lime potential: 2. Relation between the lime potential and percent base saturation of negatively charged clays in aqueous salt suspensions. Soil Sci. 94:58–63. With permission of Wolters Kluwer Health.)

19.6 Proton and Al Exchange in Silicate Clays

Ion exchange reactions on permanent charge sites in silicate clays can contribute to pH buffering (for a detailed discussion of ion exchange in clays see Chapter 16). The pH buffering by permanent charge on clays can involve exchange of hydronium ions, H_3O^+, but the exchange of Al^{3+} is much more significant.

High-activity clays; smectites, vermiculites, and illites, when saturated with H^+ have very low pH values and are not stable. When montmorillonite, a smectite, is saturated with H^+ the pH is less than 3.5. After 24 h of aging, acid dissolution of the clay structure produces Al^{3+} ions resulting in an increase in pH and replacement of the exchangeable H^+ ions with Al^{3+} (Coleman and Craig, 1961). Aluminum clays are proton donors because of the ability of Al^{3+} on clay exchange sites to hydrolyze and to precipitate as $Al(OH)_3$, but they are weaker proton donors than H^+ clays. Extraction of acid soils with neutral salt solutions, for example, 1 M KCl, yields mostly Al^{3+} not H^+ (Thomas and Hargrove, 1984).

Titration of Al^{3+} montmorillonite (Figure 19.5) shows that at $pH_{(H_2O)}$ values in the range of 5–6, the Al^{3+} on permanent charge sites strongly buffers pH (Turner and Nichol, 1962). Data in Figure 19.5 also show that as in soil, the measured pH in $CaCl_2$ is lower than the pH in water.

When base is added to an Al^{3+}-saturated smectite or vermiculite, the initial reaction is the hydrolysis of Al cations on exchange sites (Bloom et al., 1977), but with sufficient addition of strong base, the Al^{3+} will eventually precipitate as $Al(OH)_3$ in the interlayer space in the clay, accounting for much of the clay-mediated buffering at pH > 5. Because of OH^- deficiencies in interlayer $Al(OH)_3$, the interlayer can neutralize the negative charge on the clay. In the case of smectite, this produces hydroxy interlayer smectite (HIS), and in the case of vermiculite, this produces hydroxy interlayer vermiculite (HIV) (Chapter 21). Because the precipitation of interlayer $Al(OH)_3$ blocks Al^{3+} in the interlayer from reacting with the base, the titration end point in Figure 19.5 is less than the CEC of the clay, which is 800 mmol$_c$ kg^{-1}.

As with SOM, buffering in Al^{3+}-saturated clays can be described as function of BS, assuming that both H^+ and Al^{3+} are acid cations and that Al^{3+} cations represent 3 mol of acidity per mole of Al^{3+}. This is a usable generalization at pH values high enough for Al^{3+} to hydrolyze and act like an acid cation. In contrast, studies of very acidic surface soils from northern temperate forests have shown that at pH values less than 4.5, Al^{3+} should be treated as a base cation (Skyllberg, 1994; Ross et al., 2008).

The capacity of silicate clays to buffer pH varies widely because of the large difference in the CEC of clays (Table 19.2). Kaolinite, a low-activity clay, has little or no permanent charge and has little capacity to buffer pH (Chapter 21). Illite has a much greater CEC and is a much more effective buffer of pH. Smectites and vermiculites are even more effective in buffering pH. Among the silicate clays, only the highest charge vermiculites approach the buffer capacity of SOM.

19.7 pH-Dependent Charge Buffering by Mineral Components

Like SOM, oxides and hydroxides of Fe(III) and Al, and poorly crystalline aluminosilicates, contribute to the pH-dependent charges in soil and to pH buffering. In addition, the edges of

crystalline silicate clays make a minor contribution to pH-dependent charge (Chapter 16.) Unlike SOM, these materials have surfaces that are both proton donors and proton acceptors.

19.7.1 Oxides and Hydroxides of Iron and Aluminum

The oxides and hydroxides of Fe(III) and Al that accumulate in response to weathering are particularly important for pH buffering highly weathered soils (Uehara and Gillman, 1982). Common iron minerals in soil include hematite (α-Fe_2O_3), goethite (α-FeOOH), and ferrihydrite ($Fe_5O_7\ 4H_2O$) (Chapter 22). By far the most common aluminum hydroxide mineral is gibbsite, $Al(OH)_3$. In water, the hydrated surfaces of these oxides and hydroxides contain strongly bound OH groups that can act both as proton donors and proton acceptors. For hematite, the surface hydration reaction is

$$\text{Surface } Fe_2O_3 + 3H_2O = \text{Surface } 2Fe(OH)_3. \qquad (19.18)$$

The strong bonding of the O atom to Fe(III) and Al weakens the bond of the proton to the O atom, making the surface-OH groups weakly acidic and at high pH, the metal-bound hydroxide groups can donate proton creating negative surface charges (McBride, 1994):

$$\text{Surface FeOH} = \text{Surface FeO}^- + H^+. \qquad (19.19)$$

This reaction can also be written as an adsorption of OH^-:

$$\text{Surface FeOH} + OH^- = \text{Surface FeO}^- + H_2O. \qquad (19.20)$$

Also these surface-OH groups can accept protons at low pH to become positively charged:

$$\text{Surface FeOH} + H^+ = \text{Surface FeOH}_2^+. \qquad (19.21)$$

Surface adsorption of H^+ and OH^- is quantified by titrating oxide suspensions in Na^+ or K^+ salts of anions that do strongly adsorb to the oxide surfaces (e.g., NO_3^-). The data of Parks and de Bruyn (1962) illustrate typical titrations for oxide suspensions (Figure 19.6). These data show the effects of increasing KNO_3 concentration on the quantity of H^+ or OH^- adsorbed. McBride (1994) explains this effect, in a KNO_3 solution, as due to K^+ displacement of H^+ at high pH and the NO_3^- displacement of OH^- at low pH. At pH values less than 7, the oxides and hydroxides of Al and Fe are positively charged, and these surfaces are anion exchangers while at pH greater than 9 they are cation exchangers. At pH values in the range of 7–9, a point is found where the concentration of salt in solution has no effect on the pH. This is the point at which the net charge on the surface is zero; the point of zero net charge (pznc, also called the point of zero salt effect). For oxides and hydroxides of iron and aluminum, almost all measured pznc values are in the range of 7–9 (Chapter 15), meaning that unlike silicate clays and organic matter the net surface charge of these materials is positive in all except alkaline pH soils.

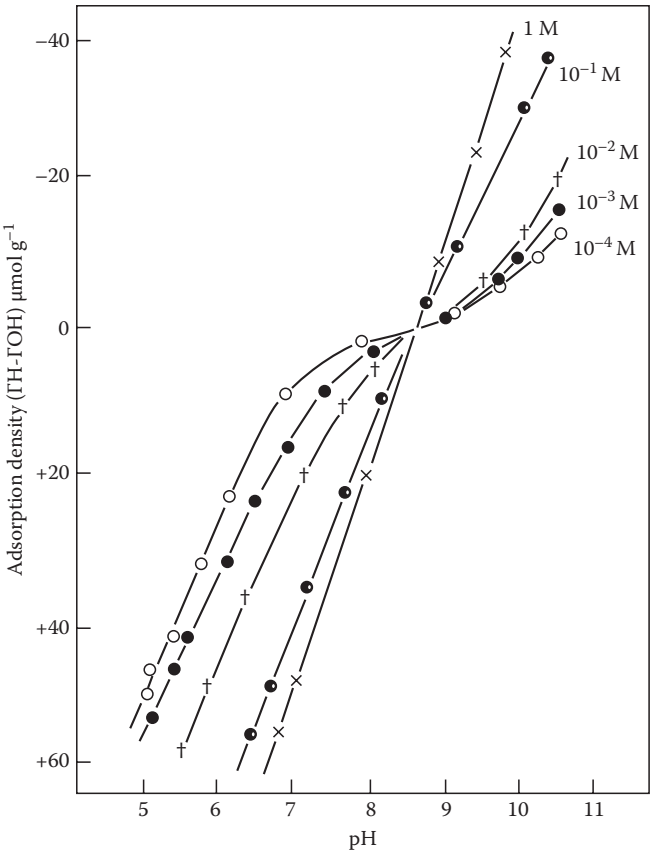

FIGURE 19.6 Titration of Fe_2O_3 with KOH and HNO_3 in suspensions containing different concentrations of KNO_3. (With permission from Parks, G.A., and P.D. de Bruyn. 1962. The zero point of charge of oxides. J. Phys. Chem. 66:967–963. Copyright 1962 American Chemical Society.)

19.7.2 pH-Dependent Charges on Silicate Clay Edges

The layer structure of silicate clays includes an AlOH layer with exposed hydroxyl groups on the edges of the structure (McBride, 1994). These Al hydroxyl groups can adsorb or desorb protons, but because of the influence of the Si^{4+} ions in the structure, the pznc is lower than for gibbsite. For example, a reported value for the pznc for the edge of kaolinite is 2.9 (Chapter 15). This means the edge charge can contribute to the negative charge in soils. For high-charged clays like smectites and vermiculite, this edge charge is small compared to the permanent structural charge. For example, for a smectite at pH 8, the pH-dependent negative charge is about 50 $mmol_c\ kg^{-1}$ compared to a permanent charge of about 750 $mmol_c\ kg^{-1}$ (McBride, 1994).

19.7.3 Imogolite and Allophane

Allophane and imogolite are aluminosilicates that like silicate clay edges have pH-dependent charge surfaces. Allophane is noncrystalline, not having long-range ordering in the structure,

and imogolite, which forms long tubes (Chapter 23; Wada, 1989) is a paracrystalline mineral with some disorder in the structure. Both of these materials are found in abundance in young volcanic soils. They are also found in some young soils in glacial parent material (e.g., spodosols in northern forests). Imogolite and allophane have pznc values in the range of 5.5–7 (Clark and McBride, 1984; Wada, 1980).

19.8 Buffering by Dissolution and Precipitation of Carbonates

Carbonates are very important for pH buffering in nonacid soils. Calcite, $CaCO_3$, and dolomite, $CaMg(CO_3)_2$, are common components of soil parent materials in many soils. With sufficient rainfall and good drainage, these minerals weather from soils. In arid regions and in some areas in humid regions with poor drainage, however, $CaCO_3$ can accumulate in soils (Chapter 30; Doner and Lynn, 1989). Under some conditions in arid regions, $MgCO_3$, which is much more soluble than calcite, can accumulate. Calcite acts as proton acceptor according to

$$CaCO_3 + 2H^+ = Ca^{2+} + H_2O + CO_2$$
$$\log K = 9.73 \quad \text{(Stumm and Morgan, 1996).} \tag{19.22}$$

The equilibrium equation for this reaction is

$$K = (Ca^{2+})\frac{(P_{CO_2})}{(H^+)_2}. \tag{19.23}$$

Calculation of this equilibrium requires knowledge of the CO_2 content in the soil atmosphere, expressed in units of partial pressure (P). At 1 atm total pressure, the value of partial pressure is equivalent to the volume fraction in the air. This equilibrium, rewritten in a form that shows how $CaCO_3$ weathers from calcareous soils, is

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^- \quad \log K = -7.42. \tag{19.24}$$

In soils, the CO_2 produced by soil microbial and root respiration dissolves $CaCO_3$ to produce calcium bicarbonate and over time $CaCO_3$ will weather out of well-drained soils.

The pH in soils that contain calcite varies widely. In a $CaCO_3$ suspension in distilled water in equilibrium with the ambient atmosphere ($P_{CO_2} \approx 3.8 \times 10^{-4}$ atm) will contain two bicarbonate ions in solution for every Ca^{2+} ion and the pH will be 8.3 (Stumm and Morgan, 1996). Because the P_{CO_2} in soils is greatly increased due to microbial and root respiration, soil solution in equilibrium with calcite will have pH values considerably lower than 8.3 (Inskeep and Bloom, 1986). The effect of P_{CO_2} on soil pH varies due to differences in the rate of soil respiration and the rate of gas exchange with the atmosphere. Gas exchange varies with depth and quantity of air-filled pores in a soil, and P_{CO_2} increases with depth and after rainfall fills soil pores with water (Flechard et al., 2007). Inskeep and Bloom (1986) showed that in pots with growing soybean plants the P_{CO_2} ranged from 0.0006 atm in drier soils to 0.031 atm at moisture contents approaching saturation. By the principle of Le Chatelier (the mass action principle), Reaction 19.22 will be shifted to the left when P_{CO_2} is raised, resulting in an increase in (H^+) and a decrease in pH.

In soils, bicarbonate concentrations are commonly not equal to twice the concentration of Ca^{2+} because there can be other sources of HCO_3^- and Ca^{2+} than dissolution of calcite by carbonic acid. When the chemistry of a calcareous soil is dominated by calcium salts other than bicarbonate, $2[Ca^{2+}]$ can be much greater than $[HCO_3^-]$ and pH is much less than 8.3, even at low P_{CO_2}. Thus, calcareous soils containing gypsum ($CaSO_4 \cdot 2H_2O$), where $[Ca^{2+}]$ is elevated by gypsum solubility, pH can be as low as 7.0. In some arid regions, input of Mg^{2+}, Na^+, and HCO_3^- results in concentrations of HCO_3^- much greater than twice $[Ca^{2+}]$ and calcareous soils can have pH values as high as 9.5. In arid regions, where Mg accumulates, and hydrated $MgCO_3$ forms, pH is greater than 8.5 because magnesium carbonate is much more soluble than $CaCO_3$.

Calcareous soils are very strongly buffered against acidification. One kilogram of $CaCO_3$ can neutralize 20,000 mmol of H^+ and hold pH at a value greater than 7 until all of $CaCO_3$ is dissolved. Thus, $CaCO_3$ is a much more effective buffer than SOM or any other component in soil (Table 19.2). If $CaCO_3$ is compared with SOM on the basis of buffering against a decrease in pH from 8.0 to 7.0, the difference is even greater than shown in Table 19.2. This pH drop would result in the total dissolution of $CaCO_3$ but would only neutralize about 200 $mmol_c$ kg^{-1} of SOM, about one-tenth of the total buffer capacity of SOM. Because of the high buffer capacity of the $CaCO_3$, calcareous soils are considered to be unaffected by acid rain and it is generally considered impractical to artificially lower the pH of calcareous soils to allow for the growth of acid-loving plants.

19.9 H^+ Consumption by Irreversible Weathering of Aluminous Minerals

The buffering reactions discussed above are all reversible and can to some degree be described using equilibrium equations. Some reactions that consume H^+ in soils, however, are irreversible. These reactions include the weathering of primary aluminosilicate minerals and the destruction of high-activity clays in very low pH soils.

19.9.1 Weathering of Primary Silicates

Over the very long term, the weathering of primary aluminosilicate minerals from soil parent material consumes protons (Chapter 20). These reactions are irreversible for most primary minerals because these minerals only form at the high temperatures involved in rock-forming processes. An example of the weathering of a primary mineral is the reaction of the feldspar

anorthite to form kaolinite in acid soils. This reaction consumes two protons for every mole of calcium mobilized:

$$\underset{\text{anorthite}}{CaAlSiO_8} + H_2O + 2H^+ \rightarrow \tfrac{1}{2}\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + Ca^{2+}. \quad (19.25)$$

The rates of weathering reactions depend on the type of primary mineral and the surface area exposed to soil solutions (Bloom and Nater, 1991). This means that, per unit mass, silt-sized particles weather much more rapidly than sand-sized particles. The rates of aluminosilicate dissolution reactions are pH dependent and at pH values typical in soils, aluminosilicates dissolve more rapidly at lower pH (Bloom and Nater, 1991; Sposito, 2004). Over time periods of less than decades, weathering of primary silicate minerals is generally not significant in buffering pH.

19.9.2 H^+ Consumption by the Destruction of High-Activity Clay

When the $pH_{(H_2O)}$ of a soil is decreased to values less than about 3.5, high-activity clays can dissolve quite rapidly consuming protons and releasing Al^{3+} into solution. As discussed in Section 19.6, H^+-saturated high-activity clays have pH values less than 3.5 and dissolve to release Al^{3+}. At this pH, $Al(OH)_3$ is too soluble to form in soils and kaolinite forms slowly, so high-activity clays tend to dissolve congruently (no solid phase is formed in the reaction). For a Ca^{2+} montmorillonite

$$Ca_{0.167}(Al_{1.67}Mg_{0.333})Si_4O_{10}(OH)_2 + 6H^+ + 4H_2O \rightarrow 0.167Ca^{2+} + 0.167Mg^{2+} + 1.67Al^{3+} + 4Si(OH)_4 \quad (19.26)$$

where five of the six protons consumed are due to the release of Al^{3+} from the structure of the clay. This reaction likely accounts for much of the very strong buffering at pH 3.5 that was observed by Magdoff and Bartlett (1985) when they added H_2SO_4 to soils (Figures 19.1 and 19.3).

19.10 Determination of Buffer Capacities

The determination of the capacity of soils to buffer pH has long been an interest of soil chemists. Many crops respond positively to the addition of lime to acid soils, but because of the differences in buffer capacity, soils of similar pH may require vastly different quantities of lime to yield the same increase in pH. Horticulturists have also been concerned with decreasing the pH of nonacid soils and they use aluminum sulfate or elemental S to allow for the vigorous growth of acidophilic plants (e.g., azaleas, rhododendron, and blueberries). As with liming, the quantity of acidifying agent necessary to lower the pH of a soil by a given amount depends on the buffer capacity. Also, acid rain can negatively impact poorly buffered forest soils and the acidifying effects depend on the capacity of soils to buffer the long-term input of very dilute HNO_3 and H_2SO_4 (Bloom and Grigal, 1985; Ulrich, 1991; Watmough and Dillon, 2004).

19.10.1 Total Titratable Acidity

The total acidity in acid soils is operationally defined as consisting of two components, salt-replaceable (exchangeable) and residual (nonexchangeable) acidity (SSSA, 2008). Salt-replaceable acidity is the H^+ and Al^{3+} extractable with 1 M KCl, while the residual acidity is the acidity that is titratable in a soil suspension but is not easily replaceable with KCl (Bertsch and Bloom, 1996). In practice, the residual acidity is determined by the difference between the total acidity neutralized by raising the pH of a soil to a reference pH, usually 7.0 or 8.0, and the salt-replaceable acidity.

Total acidity can be determined by the titration of a soil suspension in a salt solution to the reference pH using a strong base or by the addition of increments of $CaCO_3$ as shown in Figure 19.1. This produces a plot of the pH vs. the quantity of base consumed, but the response to titration with strong base and to $CaCO_3$ additions is slow, and other laboratory methods are usually used. A standard method for relatively rapid determination of total acidity is to react a soil for several hours or overnight with a solution containing 0.5 M $BaCl_2$ plus a triethanolamine (TEA) buffer adjusted to pH 8.0 or 8.2 (Thomas, 1982). TEA is well buffered at pH 8 and the solution contains Ba^{2+} to displace acidity from soil components. A reference pH of 8.0 or 8.2 is used to represent the pH attained when a soil is limed with excess lime. From a more fundamental point of view, pH 8 is a good choice because this is the end point for the titration of organic carboxyl acidity, as well as the Al^{3+} acidity bound to clays. With the $BaCl_2$–TEA method, the total acidity is calculated as the difference in the quantity of H^+ needed to titrate the $BaCl_2$–TEA solution to a pH of about 5, using a pH indicator dye, before and after reaction with a soil. This difference represents the quantity of acidity that reacts with the TEA buffer.

An alternative method for the calculation of total acidity is the difference between the CEC determined at pH 7.0 with ammonium acetate and the sum of exchangeable bases. Determination of CEC at pH 7.0 is the method most often used in the classification of soils (Burt, 2004). In this method, soil is reacted with an ammonium acetate solution at pH 7.0, the excess ammonium acetate is leached from the soil, and the NH_4^+ ions bound to cation exchange sites are extracted with a salt solution and quantified (Sumner and Miller, 1996; Burt, 2004). Subtraction of the exchangeable bases from the pH 7.0 CEC represents the total acidity referenced to pH 7.0.

19.10.2 Lime Requirement

Development of the recommendations to growers for the liming of an acid soil with ground calcitic or dolomitic limestone (agricultural lime) requires a quick and easy method for the

determination of the quantity of base needed to raise the soil pH to an optimum value for a given crop (Bloom et al., 2005; Fageria and Baligar, 2008). Because crops differ in sensitivity to soil acidity, recommendations for liming may differ with crop. The most common methods used in the United States involve the reaction of a mixed buffer solution with a soil and after a period of reaction, measurement of the equilibrium pH (Godsey et al., 2007). The commonly used Mehlich method uses a mixed buffer solution containing acetate, glycerophosphate and TEA, in $BaCl_2$, that provides for a linear buffer response to acidity at pH values ranging from 4 to 6.5 (Mehlich, 1976; Hoskins and Erich, 2008). This solution has been modified by replacing the Ba with Ca to avoid the use of toxic substances (Godsey et al., 2007; Hoskins and Erich, 2008). The pH of the buffer mixture is adjusted to 6.5 and the lime requirement is determined from the pH after reaction with a soil using regression equations for different target pH values. At lower equilibrium pH, the lime requirement is greater. The regression equations are developed using the pH response of acid soils to known additions of $CaCO_3$ (Hoskins and Erich, 2008). Hoskins and Erich (2008) showed that the inclusion of a soil $pH_{(H_2O)}$ term increased the correlation coefficient of the regression. The Shoemaker–McLean–Pratt (SMP) mixed buffer method is also commonly used (McLean et al., 1977), but this method is decreasing in acceptance because it contains two toxic buffers, *p*-nitrophenol and chromate, and tends to cause plugging of liquid junctions of pH electrodes (Hoskins and Erich, 2008). Other mixed buffer methods for determination of lime requirement include those of Adams and Evans (1962), Woodruff (1948), and Nômmik (1983).

In areas of the world where highly weathered soils are dominant, it is common to base lime recommendations on the reduction of Al^{3+} saturation of the effective CEC, calculated as the sum of bases plus 1 M KCl extractable acidity (Fageria and Baligar, 2008). When lime is added, Al^{3+} precipitates to form insoluble $Al(OH)_3$, decreasing Al^{3+} toxicity. To determine the lime requirement, the 1 M KCl replaceable Al^{3+} acidity is calculated as three times the molar quantity of extracted Al and this acidity, expressed in units of $cmol_c\ kg^{-1}$, is multiplied by a factor to calculate the lime requirement in $Mg\ ha^{-1}$. The factor varies from 1, or less, in sandy soils to greater than 3 in very clayey soils. Also an adjustment for exchangeable Ca^{2+} and Mg^{2+} is used to yield a lime requirement, even for low acidity soils, if a soil is low in Ca and Mg. These two ions are often deficient for plant growth in highly weathered soils (Fageria and Baligar, 2008).

19.10.3 Calcium Carbonate Concentrations in Soil

The quantity of calcium carbonate in soils is generally determined by methods that measure the CO_2 evolved after adding acid or the weight loss due to CO_2 loss. In the weight loss method, carefully weighed soil samples are added to weighed flasks containing 3 M HCl and loosely covered with a rubber stopper (Loeppert and Suarez, 1996). The flask is swirled and uncovered periodically until all of the CO_2 is evolved and the flask is carefully reweighed. The content of carbonate is calculated assuming all of the carbonate is $CaCO_3$ with a formula weight of $100\ g\ mol^{-1}$. For soils that have less than 2% or 3% carbonate, the weight loss method is not accurate (U.S. Salinity Laboratory Staff, 1954; Loeppert and Suarez, 1996).

Determination of the evolved CO_2 provides a more accurate and precise measure of calcium carbonate (Loeppert and Suarez, 1996). Commonly used methods involve the determination of the pressure increase in a closed cell using an Hg manometer or pressure transducer CO_2 (Williams, 1949; Martin and Reeve, 1955; Skinner et al., 1959; Evangelou et al., 1984) or the gravimetric determination of CO_2 collected in a magnesium perchlorate trap (Loeppert and Suarez, 1996).

19.10.4 Determination of the Buffering of H^+ Inputs in Noncalcareous Soils

Routine laboratory methods have not been developed for the determination of the capacity of soils to buffer against acidification. However, addition of increments of acid with long-term incubation, as used by Magdoff and Bartlett (1985), can be used to determine the response of soils to acid additions (Figures 19.1 and 19.4). An alternative method is to equilibrate soil suspensions repeatedly with dilute acid. Bloom and Grigal (1985) suspended soils in 2.5×10^{-4} M H_2SO_4 for 24 h decanted and repeated 13 times. By measuring the pH of the equilibrated solutions, they were able to determine the quantity of protons adsorbed due to pH buffering in the soil. They were also able to determine the Al^{3+} and base cation losses in each treatment. This method much more closely simulates the response to acidic deposition (acid rain) with the resultant loss of bases and Al^{3+}. Bloom and Grigal (1985) used their plots of pH response to acid to test a numerical model for the response of soils to acidic deposition.

19.11 Soil Acidification

Soil acidification occurs as a natural process during soil formation. With sufficient inputs of acid rain to poorly buffered soils, natural acidification can be very significantly accelerated (Bloom and Grigal, 1985; Ulrich, 1991). Much more rapid acidification is produced by the addition of ammonium-forming nitrogen fertilizers. Even more rapid acidification is produced by the oxidation of sulfur and sulfur compounds added to soils or of sulfur compounds deposited by natural processes in coastal wetland soils that are exposed to oxidation when the water table is lowered by artificial drainage.

19.11.1 Natural Acidification

Under conditions of good drainage and rainfall sufficient to produce leaching, H_2CO_3 and soluble organic acids cause the very slow acidification of soils that occurs during natural soil weathering. At pH values of about 6 and greater, the donation of protons by the reaction of H_2CO_3 to produce HCO_3^- (Reaction 19.13) is the predominant acidifying reaction. As the pH is

decreased to values much lower than the pK_a (6.35), H_2CO_3 is a less effective proton donor and organic acids, having lower pK_a values, are the predominant proton donors. In calcareous soils, $CaCO_3$ dissolution buffers the pH at values greater than 7 until it is all leached from the soil.

19.11.2 Acid Rain

The dry aerosol and wet acid deposition that makes up what is popularly called acid rain contains sulfuric and nitric acid plus NH_4^+ that can be oxidized in soil to produce nitric acid (Sparks, 2003). Under preindustrial conditions, these acids were of minor importance in determining the composition of soil solutions. Industrialization has resulted in elevated strong-acid acidity in rainfall, which can have long-term negative impacts on poorly buffered soils in forests and other natural areas (Bloom and Grigal, 1985; Ulrich, 1991). Since the concentration of acidic components of acidic deposition is small compared to soil buffering, even in poorly buffered soils, soil acidification is difficult to document by field-based observations and contradictory results have been reported (Courchesne et al., 2005). One of the major difficulties is the spatial variability in soil properties (Likens et al., 1998). Studies that have shown significant soil acidification that appears to be due to acid rain include the work of Courchesne et al. (2005), who reported a statistically significant decrease in pH in the humus layer of soil collected from 1993 to 2002 and Watmough and Dillon (2004), who reported a depletion of exchangeable Ca for soil collected from 1983 to 1999. Both of these studies were conducted in forests of eastern Canada.

19.11.3 Acid-Producing Fertilizers

Nitrogen fertilizers that produce NH_4^+ in soils; ammonium sulfate, ammonium nitrate, anhydrous ammonia, and urea, acidify soils. In soil, bacteria oxidize NH_4^+ to nitrate producing H^+ (Chapter 23; Havlin et al., 2005):

$$NH_4^+ + O_2 \rightarrow NO_4^- + 2H^+ + 2H_2O. \qquad (19.27)$$

This reaction can produce sufficient acidification to require periodic addition of lime to cropland (Adams, 1984).

19.11.4 Acidification by Sulfur Compounds

Sulfuric acid produced in acid mine wastes or when the soils of coastal swamps are drained, can have a large impact on soils. When pyrite or iron sulfide associated with a seam of coal or a coastal organic soil is exposed to air, bacterial oxidation results in the production of sulfuric acid (McElnea et al., 2002; Sparks, 2003):

$$\underset{\text{pyrite}}{FeS_2} + {}^{15}\!/_{4}\,4O_2 + {}^{7}\!/_{2}\,H_2O = Fe(OH)_3 + 2H_2SO_4. \qquad (19.28)$$

Under these conditions, soil pH values of less than 3 are possible. This reaction has produced large areas of acid sulfate soils in Vietnam, Malaysia, and Indonesia (Sanchez, 1976).

Acidification of nonacid soils for the growth of acid-loving (acidophilic) plants can be accomplished using elemental S. Bacterial oxidation produces a similar effect as for the oxidation of pyrite (Slaton, 2001):

$$S + {}^{3}\!/_{2}\,O_2 + H_2O = H_2SO_4. \qquad (19.29)$$

Growers using elemental S must be very careful because pH values of 3.5 are easily attainable when excess sulfur produces too much sulfuric acid (Leitzke and Peterson, 1987) (Figure 19.4).

An alternative method is to add aluminum sulfate, $Al_2(SO_4)_3$, which produces acidity according to the reaction:

$$Al_2(SO_4)_3 + 6H_2O = 2Al(OH)_3 + 3H_2SO_4. \qquad (19.30)$$

The lower pH generated by aluminum sulfate is limited by the solubility of $Al(OH)_3$ and pH will not be decreased below about 4.5 but excessive aluminum sulfate can induce Al^{3+} toxicity problems for plant growth (Leitzke and Peterson, 1987).

References

Adams, F. 1984. Crop response to lime in the southern United States, p. 211–265. *In* F. Adams (ed.) Soil acidity and liming. No. 12 Agronomy. ASA, Madison, WI.

Adams, F., and C.E. Evans. 1962. A rapid method for measuring of lime requirement of red–yellow podzolic soils. Soil Sci. Soc. Am. Proc. 26:355–357.

Andrews, J.A., and W.H. Schlesinger. 2001. Soil CO_2 dynamics, acidification, and chemical weathering in a temperate forest with experimental CO_2 enrichment. Global Biogeochem. Cy. 15:149–162.

Anon. 2008. State of the climate in 2007. Bull. Am. Meteorol. Soc. 89:S6–S102.

Bertsch, P.M., and P.R. Bloom. 1996. Aluminum, p. 517–549. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI.

Bloom, P.R., and D.F. Grigal. 1985. Modeling soil response to acidic deposition in non-sulfate adsorbing soils. J. Environ. Qual. 14:481–495.

Bloom, P.R., M.B. McBride, and B. Chadbourne. 1977. Adsorption of aluminum by smectite: I. Surface hydrolysis during Ca^{2+}–Al^{3+} exchange. Soil Sci. Soc. Am. J. 41:1068–1073.

Bloom, P.R., M.B. McBride, and R.M. Weaver. 1979. Aluminum organic matter in acid soils: Salt extractable aluminum. Soil Sci. Soc. Am. J. 43:813–815.

Bloom, P.R., and E.A. Nater. 1991. Kinetics of dissolution of oxide and silicate minerals, p. 151–189. *In* D.L. Sparks and D.L. Suarez (eds.) The kinetics of physicochemical processes in soils. SSSA, Madison, WI.

Bloom, P.R., U.L. Skyllberg, and M.E. Sumner. 2005. Soil acidity, p. 411–460. *In* A. Tabatabai and D. Sparks (eds.) Chemical processes in soils. SSSA, Madison, WI.

Borggaard, O.K. 1983. Effect of surface area and mineralogy of iron oxides on their surface. Clay. Clay Miner. 31:230–232.

Burt, R. (ed.). 2004. Soil survey laboratory methods manual. Soil survey investigations. Report No. 42. Version 4.0. Available at ftp://ftp-fc.sc.egov.usda.gov/NSSC/Lab_Methods_Manual/SSIR42_2004_view.pdf (accessed on April 26, 2011)

Clark, C.J., and M.B. McBride. 1984. Cation and anion retention by natural and synthetic allophane and imogolite. Clay. Clay Miner. 32:291–299.

Coleman, N.T., and D. Craig. 1961. The spontaneous alteration of hydrogen clay. Soil Sci. 91:14–18.

Coleman, N.T., D.E. Williams, T.R. Nielson, and H. Jenny. 1951. On the validity of interpretations of potentiometrically measured soil pH. Soil Sci. Soc. Am. Proc. 15:106–110.

Courchesne, F., B. Cote, J.W. Fyles, W.H. Hendershot, P.M. Biron, A.G. Roy, and M.C. Turmel. 2005. Recent changes in soil chemistry in a forested ecosystem of Southern Quebec, Canada. Soil Sci. Soc. Am. J. 69:1298–1313.

Doner, H.E., and Lynn, W.E. 1989. Carbonate, halide, sulfate, and sulfide minerals, p. 279–330. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. Soil Sci. Soc. Am., Madison, WI.

Essington, M.E. 2004. Soil and water chemistry. CRC press, Boca Raton, FL.

Evangelou, V.P., L.D. Whittig, and K.K. Tanji. 1984. An automated manometric method for the quantitative determination of calcite and dolomite. Soil Sci. Soc. Am. J. 48:1236–1239.

Fageria, N.K., and V.C. Baligar. 2008. Ameliorating soil acidity of tropical oxisols by liming for sustainable crop production. Adv. Agron. 99:345–399.

Fernandez, I.J., and P.A. Kosian. 1987. Soil air carbon dioxide concentrations in a New England spruce-fir forest. Soil Sci. Soc. Am. J. 51:261–263.

Flechard, C.R., A. Neftel, M. Jocher, C. Ammann, J. Leifeld, and J. Fuhrer. 2007. Temporal changes in soil pore space CO_2 concentration and storage under permanent grassland. Agric. For. Meteorol. 142:66–84.

Godsey, C.B., G.M. Pierzynski, D.B. Mengel, and R.E. Lamond. 2007. Evaluation of common lime requirement methods. Soil Sci. Soc. Am. J. 71:843–850.

Hargrove, W.L., and G.W. Thomas. 1982. Titration properties of Al-organic matter. Soil Sci. 134:216–225.

Havlin, J.L., J.D. Beaton, S.L. Tisdale, and W.L. Nelson. 2005. Soil fertility and fertilizers, 7th Ed. Prentice Hall, Upper Saddle River, NJ.

Helling, C.S., G. Chesters, and R.B. Corey. 1964. Contribution of organic matter and clay to soil cation-exchange capacity as affected by the pH of the saturating solution. Soil Sci. Soc. Am. Proc. 28:517–520.

Hoskins, B.R., and M.S. Erich. 2008. Modification of the Mehlich lime buffer test. Commun. Soil Sci. Plant Anal. 39:2270–2281.

Inskeep, W.P., and P.R. Bloom. 1986. Kinetics of calcite precipitation in the presence of water soluble organic ligands. Soil Sci. Soc. Am. J. 50:1167–1172.

Leitzke, D.A., and D.V. Peterson. 1987. Effects of soil acidification and chemical and mineralogical properties of a limed soil. Soil Sci. Soc. Am. J. 51:620–625.

Likens, G.E., C.T. Driscoll, D.C. Buso, T.G. Siccama, C.E. Johnson, G.M. Lovett, W.A. Reiners, D.F. Ryan, C.W. Martin, and S.W. Bailey. 1998. The biogeochemistry of calcium at Hubbard Brook. Biogeochemistry 41:89–173.

Loeppert, R.H., and D.L. Suarez. 1996. Carbonate and gypsum, p. 437–474. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI.

Magdoff, F.R., and R.J. Bartlett. 1985. Soil pH buffering revisited. Soil Sci. Soc. Am. J. 49:145–148.

Magnusson, T. 1992. Studies of the soil atmosphere and related physical site characteristics in mineral forest soils. J. Soil Sci. 43:767–790.

Martin, S.E., and R. Reeve. 1955. A rapid manometric method for the determining soil carbonate. Soil Sci. 79:187–197.

Mason, D.D., and S.S. Obenshain. 1939. A comparison of methods for the determination of soil reaction. Soil Sci. Soc. Am. Proc. 3:129–137.

McBride, M.B. 1994. Environmental chemistry of soils. Oxford University Press, New York.

McElnea, A.E., C.R. Ahern, and N.W. Menzies. 2002. Improvements to peroxide oxidation methods for analysing sulfur in acid sulfate soils. Aust. J. Soil Res. 40:1115–1132.

McLean, E.O., J.F. Terwiiler, and D.J. Eckert. 1977. Improved SMP buffer method for determination of lime requirement of acid soils. Commun. Soil Sci. Plant Anal. 8:667–675.

Mehlich, A. 1976. A new buffer pH method for rapid estimation of exchangeable acidity and lime requirement of soils. Commun. Soil Sci. Plant Anal. 7:637–652.

Nômmik, H. 1983. A modified procedure for the rapid determination of titratable acidity and lime requirements in soils. Acta Agric. Scand. 33:337–348.

Nordstrom, D.K., and H.M. May. 1996. Aqueous equilibrium data for mononuclear aluminum species, p. 30–80. *In* G. Sposito (ed.) The environmental chemistry of aluminum. Lewis Publishers, Boca Raton, FL.

Parks, G.A., and P.D. de Bruyn. 1962. The zero point of charge of oxides. J. Phys. Chem. 66:967–963.

Ross, D.S., G. Matschonat, and U. Skyllberg. 2008. Cation exchange in forest soils: The need for a new perspective. Eur. J. Soil Sci. 59:1141–1159.

Rossel, R.A.V., and C. Walter. 2004. Rapid, quantitative and spatial field measurements of soil pH using an ion sensitive field effect transistor. Geoderma 119:9–20.

Sanchez, P.A. 1976. Properties and management of soils in the tropics. Wiley, New York.

Skinner, S.I.M., R.L. Halstead, and J.E. Brydon. 1959. Quantitative manometric determination of calcite and dolomite in soils and limestones. Can. J. Soil Sci. 39:197–204.

Skyllberg, U. 1994. Aluminum associated with a pH-increase in the humus layer of a boreal haplic podzol. Interciencia 19:356–365.

Skyllberg, U. 1999. pH and solubility of aluminium in acidic soils: A consequence of reactions between organic acidity and aluminium alkalinity. Eur. J. Soil Sci. 50:95–106.

Slaton, N.A., R.J. Norman, and J.T. Gilmour. 2001. Oxidation rates of commercial elemental sulfur products applied to an alkaline silt loam from Arkansas. Soil Sci. Soc. Am. J. 65:239–243.

Smith, R.M., A.E. Martell, and R.J. Motekaitis. 2004. NIST critically selected stability constants of metal complexes database. National Institute of Standards and Technology, U.S. Department of Commerce, Washington, DC.

Sorensen, S.P.L. 1909. Enzyme studies: II. The measurement and importance of the hydrogen ion concentration in enzyme reaction. Compt. Rend. Trav. Lab. (Carlsberg) 8:1.

Sparks, D.L. 2003. Environmental soil chemistry. Academic Press, New York.

Sposito, G. 2004. The surface chemistry of natural particles. Oxford University Press, New York.

SSSA (Soil Science Society of America). 2008. Glossary of soil science terms. SSSA, Madison, WI.

Stevenson, F.J. 1994. Humus chemistry: Genesis, composition, reactions, 2nd Ed. Wiley, New York.

Stumm, W., and J.J. Morgan. 1996. Aquatic chemistry: Chemical equilibria and rates in natural waters, 3rd Ed. Wiley, New York.

Sumner, M.E., and W.P. Miller. 1996. Cation exchange capacity and exchange coefficients, p. 1201–1229. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. SSSA Book Series 5. SSSA, Madison, WI.

Thomas, G.W. 1982. Exchangeable acidity, p. 159–165. *In* Methods of soil analysis. Part 2. Chemical methods. Chemical and microbiological properties. ASA Monograph 9. ASA, Madison, WI.

Thomas, G.W. 1996. Soil pH and soil acidity, p. 475–490. *In* Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI.

Thomas, G.W., and W.L. Hargrove. 1984. The chemistry of soil acidity, p. 3–56. *In* F. Adams (ed.) Soil acidity and liming. 2nd Ed. ASA, Madison, WI.

Turner, R.C., and W.E. Nichol. 1962. A study of the lime potential: 2. Relation between the lime potential and percent base saturation of negatively charged clays in aqueous salt suspensions. Soil Sci. 94:58–63.

Uehara, G., and G. Gillman. 1982. The mineralogy, chemistry and physics of tropical soils with variable charge clays. Westview Press, Boulder, CO.

Ulrich, B. 1991. An ecosystem approach to soil acidification, p. 28–79. *In* B. Ulrich and M.E. Sumner (eds.) Soil acidity. Springer-Verlag, Berlin, Germany.

U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvements of saline and alkali soils. USDA Handbook 60. U.S. Government Printing Office, Washington, DC.

Van Raij, B., and M. Peech. 1972. Electrochemical properties of some oxisols and alfisols of the tropics. Soil Sci. Soc. Am. Proc. 36:446–451.

Wada, K. 1980. Mineralogical characteristics of andosols, p. 87–107. *In* B.K.G. Theng (ed.) Soils with variable charge. New Zealand Soil Science Society, Lower Hutt, New Zealand.

Wada, K. 1989. Allophane and imogolite, p. 1051–1087. *In* J.B. Dixon and S.B. Weed (eds.) Minerals in soil environments. SSSA, Madison, WI.

Walker, W.J., C.S. Cronan, and P.R. Bloom. 1990. Aluminum solubility in organic soil horizons from northern and southern forested watersheds. Soil Sci. Soc. Am. J. 54:369–374.

Watmough, S.A., and P.J. Dillon. 2004. Major element fluxes from a coniferous catchment in central Ontario, 1983–1999. Biogeochemistry 67:369–398.

Williams, D.E. 1949. A rapid manometric method of the determination of carbonate in soil. Soil Sci. Soc. Am. Proc. 13:127–129.

Woodruff, C.M. 1948. Testing of lime requirement by means of a buffer solution and the glass electrode. Soil Sci. 66:53–63.